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# Relaxation processes in thiophene-based random copolymers

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**Abstract**

The relaxation dynamics of soluble polyalkylthiophenes obtained by the random copolymerisation of 3,4-dibutylthiophene and 3-butylthiophene monomers is investigated. In these systems, the effective conjugation length, the optical gap and the non-radiative decay rate are controlled by varying the content of disubstituted monomers, the steric hindrance of which induces a twisting angle between thiophene rings. Several indications are reported in favour of spectral diffusion of the photoexcitations. Migration processes mainly occur within a few tens of picoseconds. 

## 1. Introduction

Due to the flexibility of molecular design, the optical properties of thiophene-based polymers can be finely tuned by substituting the monomer with electron/acceptor groups or steric hindered side chains. In particular, polyalkylthiophenes are good candidates for obtaining light-emitting devices [1–3]. It is widely recognised that inter-ring twisting regulates the degree of conjugation and therefore the energy position of the absorption and emission spectra. With the intent of tailoring the optical properties of thiophene-based polymers, we synthesised a series of copolymers made by random distribution of 3-butyl- and 3,4-dibutylthiophene monomers in different ratios, in which the electronic properties depend on the concentration of disubstituted monomers. By varying the copolymer composition it is possible to tune both the energy and the intensity of the luminescence spectra. These copolymers also provide an excellent tool to study the incoherent motion of photoexcitations in a one-dimensional system with a controlled degree of disorder.

In this Letter we present the study of the optical properties and relaxation dynamics as a function of the fraction $f$ of the disubstituted monomer. The effects of the random alternation of the two monomers on the emission properties and migration processes along the $\pi$-conjugated chain have been analysed by several spectroscopical techniques, i.e. optical absorption, steady state and picosecond time-resolved photoluminescence (PL), transient photoluminescence anisotropy and quantum emission efficiency.

## 2. Experimental

The samples were prepared by chemical oxidative coupling using $FeCl_3$. The synthesis details and the

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sample characterisation are reported elsewhere [4]. The absorption and emission spectra were taken on copolymers dissolved in anhydrous tetrahydrofuran at concentrations lower than $10^{-4}$ M. Quantum yields were measured with a Jasco FP777 spectrofluorimeter using quinine sulphate solutions as a standard [5]. The cw photoluminescence spectra were taken using a single photon counting spectrometer and were corrected for the instrumental spectral response. The 363 nm line of an argon laser or an Xe lamp were used as excitation.

Spontaneous emission was excited by the second harmonic (390 nm) of a synchronously pumped dye-laser delivering 0.5-ps-long pulses. Spectral resolution was obtained through a monochromator. Temporal dispersion of the signal was achieved through a Hamamatsu optical sampling oscilloscope. After spectral and temporal dispersion, the resulting time resolution was 30 ps. The quantum yields and the time-resolved PL spectra were measured on the same solutions.

## 3. Results and discussion

Fig. 1 shows the absorption and cw-photoluminescence spectra of the copolymers in solution for various fractions $f$ of the disubstituted monomer. By increasing $f$, the absorption (luminescence) maximum is tuned continuously from 2.88 eV (2.17 eV) for the poly-3-butylthiophene homopolymer to 3.88 eV (2.60 eV) for the poly-3,4-dibutylthiophene homopolymer. The increase of the optical gap with the fraction $f$ has been attributed to the growing content of adjacent alkyl groups, which favours the inter-ring twisting and thus induces a reduction of the backbone conjugation length [4]. The mean number $n$ of conjugated rings can be estimated by comparing the energies of the lowest absorption peaks in our copolymers and in thiophene oligomers of different lengths [6]. This way, we find that $n$ varies from $\sim 5$ to $\sim 2$ on going from $f = 0$ to $f = 1$.

All the solutions display a large Stokes shift between absorption and emission. Part of this shift is due to the planarization of the excited state which occurs after photoexcitation [7,8]. From the mono- to the disubstituted homopolymer the Stokes shift is almost doubled, in agreement with the increasing

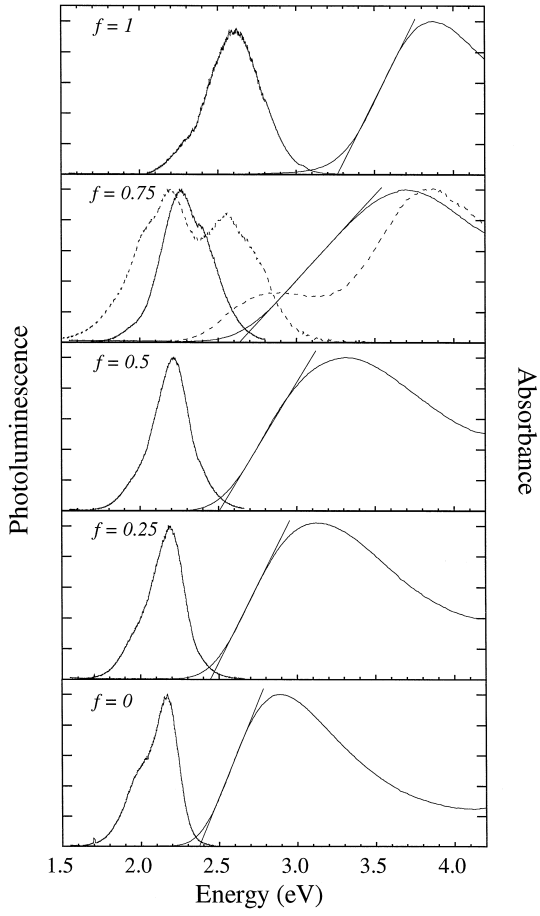


Fig. 1. Absorption and emission spectra (excited at 363 nm) of the copolymers, at various fractions $f$ of the disubstituted monomer. For $f = 0.75$ the absorption and emission spectra of the relative mixture are shown (dashed curves). The intersections of the straight lines with the energy axis define the onset of the absorption spectra.

distortion of the backbone as $f$ increases. In Fig. 1, for $f = 0.75$ we also present by way of example the absorption and photoluminescence spectra of a solution obtained by dispersing one part and three parts of the mono- and disubstituted homopolymers, respectively. Two peaks appear both in absorption and emission, their position being strictly associated to the absorption and emission response of each homopolymer. Similar results have been obtained for mixtures with different $f$. In emission, both peaks can be selectively excited by tuning the excitation wavelength close to the corresponding absorption

peak. Conversely, the emission spectra of the copolymers are almost independent of the excitation energy. These findings show that the copolymer response does not arise from the independent contributions of the mono- and disubstituted homopolymers, and indicate that there exists a distribution of conjugation lengths that is single peaked. This distribution gives rise to the inhomogeneous broadening of the absorption spectra.

In polymers with a relevant inhomogeneous broadening of the electronic states, migration of the excitations from higher towards lower energy emitting states is expected to influence the temporal behaviour of the spectrally resolved emission [9,10]. However, it is worth noting that in first approximation spectral diffusion does not influence the spectrally integrated emission. Consequently, relaxation processes different from spectral migration can be investigated by measuring the time decay of the luminescence emitted over a large spectral window. The insert of Fig. 2a reports the spectrally integrated photoluminescence decay for different $f$. The photoluminescence decay time $\tau_{PL}$, defined as the time required for the signal to reach $1/e$ of the initial value and shown in Fig. 2a, decreases from 600 ps for $f=0$ to 150 ps for $f=1$. The same figure shows that the quantum yield (QY) of the samples in solution decreases non-linearly from 0.15 to 0.04 by increasing $f$, exhibiting a behaviour similar to the decay time $\tau_{PL}$. If radiative and non-radiative decay are monomolecular processes with rates $\tau_r^{-1}$ and $\tau_{nr}^{-1}$, respectively, the photoluminescence efficiency is given by: [11] $QY = b\tau_{PL}/\tau_r$. Here $b$ represents the fraction of absorbed photons leading to the generation of singlet excitons. By reasonably taking $b=1$, [11] we have calculated $\tau_r$. As presented in Fig. 2a, $\tau_r$ changes non-monotonically from 3.3 ns for $f=0$ to 4.3 ns for $f=1$, showing a much less pronounced variation than in the case of $\tau_{PL}$. Since from the monosubstituted to the disubstituted polymers $n$ decreases from 5 to 2, $\tau_r$ should be compared with the radiative decay rate of the corresponding oligothiophenes. For quinquithiophene, $\tau_r \sim 3.4$ ns and increases non-monotonically up to 4.0 ns for $n=2$ [12]. This behaviour is similar to the one we have observed in our copolymers, justifying the assumption of considering the copolymers as a sequence of segments with short conjugation length. In

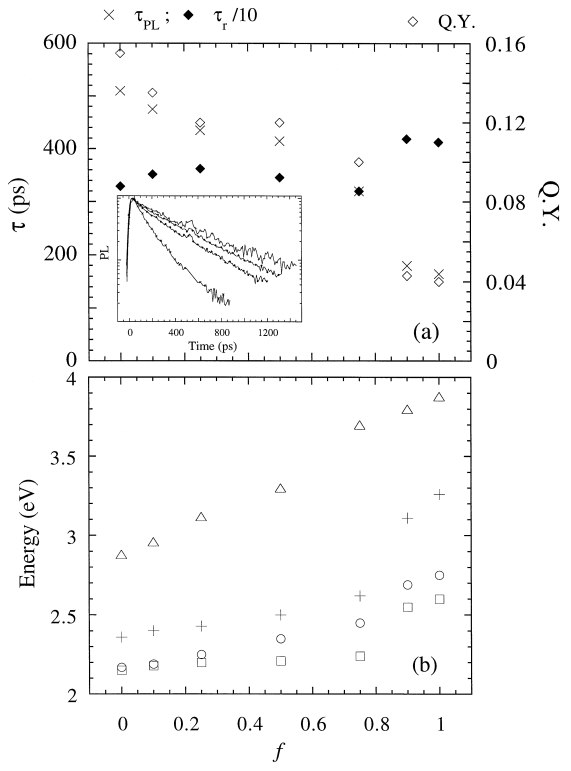


Fig. 2. (a) Photoluminescence decay time $\tau_{PL}$, radiative decay time $\tau_r$ and photoluminescence quantum yield QY, as a function of $f$. Insert: decay of the spectrally integrated photoluminescence at different $f$ (from the top to the bottom: $f=0$, $f=0.5$, $f=0.75$, $f=1$). Spectra are normalised to the maximum intensity. (b) Energy positions of the absorption maxima (triangles) and onsets (crosses), the cw-photoluminescence maxima (squares) and the photoluminescence maxima at $t=0$ (circles), as a function of $f$.

thiophene oligomers, $\tau_{PL}$ has been found to change from 700 to 50 ps when the number of rings varies between 5 and 2 [12]. This reduction of $\tau_{PL}$ by decreasing the ring number has been mainly attributed to the increasing probability for intersystem crossing [6], which is the dominant contribution to the non-radiative decay of the singlet excitations. Sophisticated calculations indicate that the intersystem crossing between the excited singlet $S_1$ and triplet $T_1$ manifolds is a two-step process, involving a quasi-resonant transfer between the $S_1$ and a higher energy triplet state $T_4$, followed by fast relaxation towards $T_1$ [6]. The decreasing intersystem crossing for longer oligomers has been attributed to the increasing energy gap between $T_4$ and $S_1$, which leads

to a slower $S_1 \rightarrow T_4$ transfer rate. $\tau_{PL}$ versus $f$ and $\tau_{PL}$ of oligothiophenes versus $1/n$ exhibit a quite similar behaviour, indicating that an analogous increase of the cross-section to the triplet manifold occurs. In conclusion, the reduction of the quantum yield with increasing $f$ has to be entirely ascribed to an increase of the non-radiative decay rate, which is correlated with the reduction of the conjugation length at high $f$.

The large variation of the energy gap and QY are the most evident effects induced by the presence of disubstituted monomers. Other features of the absorption and luminescence spectra need to be pointed out: (i) all the absorption spectra exhibit a large width. In homopolymers, the large width is mainly related to the distribution of conjugation lengths [4,13]. The inhomogeneous broadening of the optical transition in the homopolymers is consistent with the recent observation of spectral diffusion processes in these compounds [14]. For the copolymers, the absorption width is larger, since the random copolymerisation process gives rise to a larger width of the distribution of conjugation lengths; (ii) as shown in Fig. 2b, the absorption peak varies linearly with $f$, while the energy of the absorption onset (obtained as shown in Fig. 1) and the peak energy of the luminescence spectra, both temporally integrated (cw) and at zero-delay after excitation, show an appreciable deviation from the linear interpolation between the corresponding values at $f = 0$ and $f = 1$.

Before discussing these data, it is worth making some preliminary remarks on the optical response of random copolymers. Their electronic properties have been calculated in the literature following a simple tight-binding approach [13]. The calculations indicate that the difference between the maxima of the valence and conduction density of states (DOS) varies linearly on going from the low-gap to the high-gap homopolymer, in good agreement with the experiment. The random distribution of mono- and disubstituted monomers gives rise to a large distribution of conjugation length and therefore to an inhomogeneous broadening of the DOS. The broadening becomes larger for intermediate values of $f$ and consequently the energy difference between the DOS onsets varies non-linearly in agreement with our finding. Note, furthermore, that the larger deviation from the linear behaviour does not occur for $f = 0.5$, but for $f \sim 0.75$, both in the experiment (cross symbols in Fig. 2b) and in the model [13]. This effect takes its origin from the fact that fluctuations of the conjugation length with respect to the mean value are more probable when the latter is short, i.e. for a higher concentration of disubstituted monomer.

As far as the emission properties are concerned, let us remark that at time $t \approx 0$ ($\tau \ll \tau_{nr}, \tau_r$) the emission spectra, unlike the cw spectra, do not depend on the QY of the emitting center, but only on the radiative emission probability. Since this latter is weakly dependent on the substituents (see Fig. 2a), the photoluminescence intensity at $t \sim 0$ and at a given energy will monitor the occupation probability of the corresponding emitting site. Therefore, the observation that the emission maxima at $t \approx 0$ follows the behaviour of the absorption onset versus $f$ suggests that the photoexcitations, excited well above the optical gap, have migrated towards low-gap regions of the backbone (DOS tail) within our time resolution (30 ps). The relaxation rate is expected to be strongly reduced at later times, because in one-dimension the nearest-neighbour sites are only two and the probability that excitations are trapped in segments ('dead ends' [15]) surrounded by higher energy sites becomes quite large. Time-resolved PL anisotropy, presented in Fig. 3 for the representative case $f = 0.75$, substantiates this relaxation scenario. The photoluminescence anisotropy is defined as $\rho = I_{\parallel}/I_{\perp}$, where $I_{\parallel}$ and $I_{\perp}$ are the PL intensity emitted

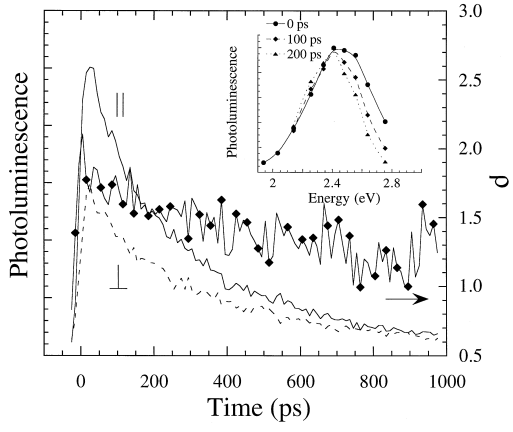


Fig. 3. Decay of the spectrally integrated photoluminescence measured parallel and perpendicular to the pump and their ratio $\rho$, for $f = 0.75$. Insert: emission spectra at different delays. Spectra are normalised to the maximum emission intensity.

with polarisation parallel and perpendicular to the incoming laser polarisation, respectively. Theoretically, the depolarisation ratio in a randomly oriented ensemble of emitters should be 3 at $t = 0$. However, we find that $\rho \sim 1.8$ within the temporal resolution of our apparatus, in agreement with the hypothesis of an initial fast spectral diffusion. The anisotropy decay at later times is much slower (lifetime ≈ 650 ps). This decay is mainly due to the motion of the chains within the solvent, which is absent when the chain mobility is inhibited [14].

Photoluminescence spectra at different delays are reported in the insert of Fig. 3, showing that a red shift of the high energy tail occurs as time elapses. Similar results are obtained for different $f$. This red shift could be ascribed to spectral diffusion processes [9,10,14]. However, the previous spectrally integrated PL transients have shown that the non-radiative decay rate is faster in segments with shorter conjugation length, which have a higher energy transition from the highest occupied to the lowest unoccupied molecular orbital (HOMO–LUMO). This additional spectral dispersion of the lifetimes is expected to contribute mostly to the red shift of the luminescence at delays comparable to and longer than $\tau_{nr}$, as migration has been shown to occur on a much shorter timescale ($< 30$ ps $\ll \tau_{nr}$).

The trend of the photoluminescence lifetime as a function of the emission energies is shown in detail in Fig. 4. $\tau_{PL}$ is shorter at higher emission energies and decreases by increasing $f$. We roughly distinguish two different behaviours of $\tau_{PL}$, followed respectively by the monosubstituted (see curve (a) in Fig. 4) and the disubstituted homopolymers (see curve (b)). We observe that: (i) copolymers with $0 < f < 0.5$ have a monosubstituted-like behaviour; (ii) for $f = 0.5$ and $f = 0.75$, $\tau_{PL}$ agrees with curve (a) at energies lower than about 2.4 eV and with curve (b) for higher energies; (iii) copolymers with $f \geqslant 0.9$ have a disubstituted-like behaviour. Point (i) provides further evidence that the largest contribution to the emission comes from sample regions electronically similar, which are mostly made up by monosubstituted units reached after the photoexcitation. Point (ii) shows that a small part of the excitations are 'frozen' on disubstituted-rich regions, i.e. they can not reach lower energy states within their lifetime.

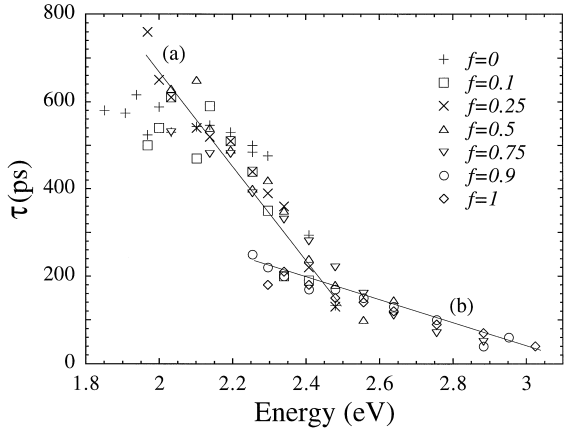


Fig. 4. Decay time of the photoluminescence measured at different energy, at various $f$. The excitation wavelength is 390 nm. Lines (a) and (b) are guides for the eye, as explained in the text.

The two-mode behaviour of the lifetime dispersion can be rationalised as follows. Since the conjugation length of the disubstituted polymers is quite short ($n = 2$), as a first approximation the disubstituted units can be seen as non-conjugated defects which break the conjugation between monosubstituted sequences [13]. The conjugated segments of different lengths ($n > 2$) are therefore made up by the sequence of monosubstituted units which are delimited by disubstituted monomers. Light emitted from these regions should exhibit the spectral dispersion lifetime typical of the monosubstituted polymer (curve (a) in Fig. 4). Finally, sequences of more than two disubstituted moieties have the same HOMO–LUMO transition energy, since the conjugation length does not vary ($n = 2$). The dispersion lifetime of the emission from these regions is that of the disubstituted polymer, and corresponds to the curve (b) in Fig. 4.

## 4. Conclusions

The emission properties of copolymers made up by the random polymerisation of 3,4-dibutylthiophene and 3-butylthiophene have been investigated. Both the emission energy and quantum emission efficiency vary with the fraction $f$ of the disubstituted monomer. The reduction of the quantum yield by increasing $f$ is related to the decrease

of the non-radiative decay time that is due to the enhanced intersystem crossing rate.

The behaviour of the emission peak at $t \approx 0$ as a function of $f$ shows that photoexcitations migrate toward segments of the polymer chain with a prevalence of monosubstituted moieties. Transient photoluminescence anisotropy data indicate that spectral migration is negligible at time longer than 30 ps.

## References

[1] D. Braun, G. Gustafsson, D. McBranch, A.J. Heeger, J. Appl. Phys. 72 (1992) 564.
[2] K. Yoshino, S. Morita, M. Uchida, K. Muro, T. Kawai, Y. Ohmori, Synth. Met. 55 (1993) 28.
[3] G. Rumbles, I.D.W. Samuel, L. Magnani, K.A. Murray, A.J. DeMello, B. Crystall, S.C. Moratti, B.M. Stone, A.B. Holmes, R.H. Friend, Synth. Met. 76 (1996) 47.
[4] M. Catellani, S. Luzzati, R. Mendichi, A. Giacometti Schieroni, Polymer 37 (1996) 1059.
[5] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.
[6] D. Beljonne, J. Cornil, R.H. Friend, R.A. Janssen, J.L. Brédas, J. Am. Chem. Soc. 118 (1996) 6453.
[7] J.L. Brédas, B. Themans, J.G. Fripiat, J.M. André, R.R. Chance, Phys. Rev. B 29 (1984) 6761.
[8] G. Lanzani, M. Nisoli, M. Magni, S. De Silvestri, G. Barbarella, G. Zambianchi, R. Tubino, Phys. Rev. B 51 (1995) 13770.
[9] U. Rauscher, H. Bässler, D.D.C. Bradley, M. Hennecke, Phys. Rev. B 42 (1990) 9830.
[10] U. Lemmer, R.F. Mahrt, Y. Wada, A. Greiner, H. Bässler, E.O. Göbel, Chem. Phys. Lett. 209 (1993) 243.
[11] N.C. Greenham, I.D.W. Samuel, G.R. Hayes, R.T. Phillips, Y.A.R.R. Kessener, S.C. Moratti, A.B. Holmes, R.H. Friend, Chem. Phys. Lett. 241 (1995) 89.
[12] Y. Kanemitsu, K. Suzuki, Y. Masumoto, Y. Tomiuchi, Y. Shiraishi, M. Kuroda, Phys. Rev. B 50 (1994) 2301.
[13] G. Lanzani, A. Piaggi, C. Botta, M. Catellani, E. Prevosti, P.C. Stein, R. Tubino, Solid State Commun. 99 (1996) 707.
[14] A. Watanabe, T. Kodaira, O. Ito, Chem. Phys. Lett. 273 (1997) 227.
[15] B. Movaghar, B. Ries, M. Grünewald, Phys. Rev. B 34 (1986) 5574.